SHIPBOARD WATER DISINFECTION AND BROMATE FORMATION

A Thesis

Presented to the Faculty of the Graduate School

of Cornell University

in Partial Fulfillment of the Requirements for the Degree of Master of Science

by

Stephanie Wood

January 2014

ABSTRACT

Many Navy and Coast Guard ships produce and disinfect their own water while underway. The preferred method of disinfection is through use of a polybrominated ion exchange resin. This study examines the relationship between shipboard disinfection manuals and EPA standards, in addition to determining whether bromate is likely to form.

Some disconnect exists between EPA standards and standards set by each service in their own disinfection manuals. The most serious of which is the pH standard, or lack thereof. Given that desalinated water is stripped of virtually everything that may react with bromine to form bromate, the easiest and most likely condition for bromate to form is through high pH--that is, pH greater than 8.0.

The Coast Guard and Navy need to update their potable water manuals to include a section on pH in order to prevent personnel from consuming water that contains the possible human carcinogen, bromate.

ACKNOWLEDGEMENTS

I would like to thank my Special Committee members for their support and patience during this unusual master's program. In particular, Prof. James J. Bisogni for his willingness to support such a strange interest as bromine and Prof. Len Lion for providing keen insight into all things chemical.

A special thank you goes to CDR Harrichand Rhambarose for encouraging my research so whole-heartedly and with the full weight of Health Safety and Work-Life office.

An additional thank you goes to CDR Peter Carroll and LCDR Cesar Acosta, without whom I would not have been afforded extra time to complete a research based degree. LT Rachael Love also deserves a hearty thank you, for putting up with me and for assisting me so extensively over the course of my graduate studies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The ability to disinfect water properly is crucial to the success of many Navy and Coast Guard surface missions. Every ship that spends any significant amount of time underway has the capacity to produce and disinfect drinking water. Hundreds of sailors depend on shipboard water resources. Ensuring proper treatment and storage of this water is critical.

Bromine is currently the preferred method of shipboard disinfection. It is easy to handle, simple to maintain, and very effective. However, bromine is not as widely understood as chlorine. Chlorine has simpler kinetics and an extensive history of municipal use. As with any disinfection method, there are several factors to be concerned with and many standards governing the use of bromine to follow. The Environmental Protection Agency (EPA), states that bromine residuals in drinking water should be kept below 1.0 ppm and pH of the water should be between 6.5 and 8.5 (RED, 1993). While naval surface ships are not required to meet EPA standards, they are generally maintained.

The following study provides a detailed look at drinking water disinfection procedures aboard surface ships (particularly U.S. Coast Guard cutters), how these procedures align with EPA recommended guidance, and whether or not bromate is likely to form given shipboard conditions and desalinated water composition.

2. BACKGROUND

2.1 Review of Shipboard Water Disinfection

When ships are moored stateside, drinking water is piped directly from the pier to the users onboard. When ships are underway for more than a few days reverse osmosis (RO) or multi-stage flash evaporation (MSF) systems are used to keep up with water demand. As fresh water is produced it is stored in large tanks and then distributed to users as needed. To prevent bacterial growth a small portion of desalinated water is disinfected prior to entering the water storage tanks.

2.2 Bromine

Prior to the 1970's bromine was not practical for shipboard use. It was common to disinfect with calcium hypochlorite (HTH). For disinfection purposes HTH is perfectly capable. However, military members execute shipboard disinfection with minimal expertise in water disinfection. The method by which HTH is added to ship's drinking water is relatively complex and usually results in over-chlorination. HTH also poses a storage challenge. It decomposes exothermically when contaminated with water or moisture from the atmosphere and can pose a potential fire hazard.

When polybrominated ion exchange resin was invented it rapidly became the most common form of shipboard disinfection. The resin is available in an easy to

use and easy to handle cartridge. The cartridge is installed and replaced at the brominator, requiring little specialized knowledge and virtually no oversight. Cartridges can be stored for up to 2 years without degradation and can be used after 2 years with some decrease in potency.

In May of 1976 Bromine was registered for use to treat potable water through a polybrominated ion exchange resin aboard Naval surface ships (EPA RED, 1993). In the same year the Environmental Protection Agency (EPA) established a food additive tolerance of 1.0 ppm residual bromine in potable water aboard ships (EPA RED, 1993). Currently, Naval ship building specifications identify two methods for disinfection -- brominators and electrolytic disinfection generator systems (nav spec ABS NVR 5-2-6/3.3.6 (2010)). The Coast Guard uses brominators exclusively.

2.2.1 Bromine Disinfection Byproducts

Again, per the EPA, residual bromine for water disinfection should not exceed 1.0 ppm. In water and in organisms, bromine reacts to form bromides. Bromides do not have an upper limit because they have been used as human drugs and thus, their health effects are well understood. The levels of bromides consumed as drugs far exceed the levels ingested from registered water purification uses. A moderate dose to treat epilepsy would be 50 mg/kg per day. The typical dose ingested through water is approximately 0.03 mg/kg per day. In addition to bromide, bromate may form as a by-product under some disinfection conditions and when the pH is greater than 8.0. Bromate has a 10 ppb (10 μg/L) maximum contaminate level (MCL) and causes several types of cancer in rats. EPA has

assigned the bromate ion to Group B2 (probable human carcinogen). Based on data collected from several U.S. Coast Guard cutters underway and producing water, users frequently receive water at a pH higher than 8.0.

2.3 Guidance on Shipboard Water Disinfection

Disinfecting water onboard Coast Guard and Navy ships is done daily and regulated by several detailed publications. At the top of the water disinfection instructions are the EPA standards, followed by the Naval Ship's Technical Manual (NSTM) chapter 533, then the Coast Guard Potable Water Manual, and lastly individual ship's potable water standard operating procedures.

2.3.1 EPA

The EPA has approved the use of bromine to treat drinking water aboard Naval ships and offshore oil platforms, with a maximum residual (MRDL) of 1.0 ppm (4 ppm for chlorine). It is suggested that measures be in place to prevent ingestion when these MRDL's are exceeded. The Navy and Coast Guard strive to meet these standards, however, are not specifically required to.

2.3.2 Naval Ship's Technical Manual

The NSTM is a massive document that provides technical information for supervision, operation and maintenance of U.S. Navy Ships and submarines. Per NSTM Chapter 533 a measurable residual trace of Free Available Chlorine (FAC) or Total Bromine Residual (TBR) shall be maintained in all parts of the potable water

system. For disinfection in a ship's tanks chlorine or bromine should be added to produce an initial concentration of 1 ppm chlorine or 0.7 ppm bromine. With this dose, the concentration after a 30 minute contact time should drop to 0.2 ppm FAC or TBR. The 30 minute contact time is the amount of time disinfectant is required to be mixed with stored water before becoming available to the distribution system. When a ship receives water from another source pH and halogen residual (FAC or TBR) should be measured. If the residual is 0.2 ppm or more and the pH is less than 8.5, no further disinfection is required. If the water composition is unknown, a dose of no fewer than 1.0 ppm chlorine or 0.7 ppm bromine shall be used initially.

According to NSTM 533 if the pH is greater than 8.5 additional disinfection is required because "high pH levels will adversely affect the disinfectant properties of chlorine and bromine." In this situation, when the pH is above 8.5 and chlorine is used the water shall be treated to provide at least 0.6 ppm FAC residual at the end of 30 minute contact period. When the pH is above 9.5 and bromine is used as the disinfect, the water shall be treated to provide at least a 0.6 ppm TBR residual at the end of the 30 minute contact period.

Disinfection practices change when a ship takes on water of "doubtful quality", that is when water is received from a source outside the United States or from an area where amebiasis or infectious hepatitis is endemic. In this situation the NSTM requires water be treated to be provide at least a 2.0 ppm FAC or TBR residual at the end of the 30 minute contact period.

The NSTM does not provide any upper or lower limits on ship water pH. NSTM Chapter 533 was last updated on 15 March 1995.

2.3.3 Coast Guard

Coast Guard specific guidance on potable water systems is in COMDTINST M6240.5 Water Supply and Wastewater Disposal Manual. Per this instruction, shipboard water in potable water tanks should be disinfected with chlorine or bromine to produce at least 0.2 ppm FAC or TBR after 30 minutes contact time. This manual does not recommend disinfecting with bromine at a level greater 2.0 ppm because these levels are not "practical due to the length of time required."

If water is received from a questionable or unapproved source, operators must chlorinate or brominate water to achieve a residual between 2.0 and 5.0 ppm FAC or TBR after a 30 minute contact time.

The Coast Guard's Water Supply and Wastewater Disposal Manual does not provide limit guidance for pH, except to state that for pH greater than 8.5 chlorine and bromine are less effective disinfectants.

2.3.4 Navy

The Navy's water disinfection guidance is found in Chapter 6 of the Manual of Naval Preventive Medicine NAVMED P-5010-6 (Rev.2-2005). Here it states that the maximum contaminant level (MCL) for all disinfectants is 4 ppm. This is correct for chloramines and chlorine, however, the MCL for chlorine dioxide is only 0.8 ppm and bromine is 1.0 ppm.

The Navy requires that water be disinfected to contain 0.2 ppm FAC or TBR after 30 minute contact time. Water received from approved sources should have at

least some halogen residual, in the event it does not, it should be disinfected to provide at least 0.2 ppm FAC or TBR. For municipalities that use chloramines in lieu of chlorine, shipboard personnel should verify that at least 2.0 ppm total chlorine residual is present.

Water from an approved source must be chlorinated or brominated to provide at least 2.0 ppm FAC or TBR after a 30 minute contact time.

2.4 Monitoring Disinfection

NSTM Chapter 533 requires that U.S. Naval Ship's routinely test for FAC or TBR by the ship's medical and engineering departments. Specifically, water should be tested prior to receipt of water, daily in potable water tanks, and water sampled from points that varied and are representative of the ship's distribution system. Engineers shall test water for residuals whenever bromine cartridges are changed, after a 30 min contact period in a potable water tank, and prior to putting a potable water tank into service. The recommended halogen residual test equipment is the bromine test equipment provided by the manufacturer at the time the brominator is installed.

2.5 Summary

Shipboard water disinfection is an important activity that occurs constantly while underway. Disinfection manuals need to be updated to reflect the most current EPA standards and sections should be added to address actions to be taken in the event water pH exceeds 8.0 (NAVMED, 2005).

3. DESALINATED WATER

To determine how bromine is converted to bromate, it is important to understand the composition of shipboard desalinated water.

3.1 Desalination Processes

The Coast Guard desalinates using one of two processes--reverse osmosis (RO) or multi-stage flash distillation (MSF) The composition of the RO and MSF distillate is virtually identical (Ludwig, 2004). Thermal distillation via an evaporator is convenient because of its durability--even a feedwater with high salinity, high temperatures, and high fouling potential is easily handled by these systems. In an optimally run RO, membranes have salt rejections greater than 99 percent (Greenlee, et. al 1999).

It is helpful to realize that desalination feedwater is significantly different from standard municipal feedwaters. Saltwater feedwater likely contains micro and macroalgae and cyanobacteria; bacteria; and chemicals that are more abundant in seawater, like boron, bromide, and chloride (WHO, 2004). Other chemical issues, such as control of additives, disinfection by-products and pesticides are similar to those encountered in fresh water, except these issues vary more widely and greater quantities may be involved in desalination (WHO, 2004).

3.2 Distillate and Permeate

Desalinated water lacks minerals typically found in drinking water and is "aggressive" towards materials used in water supply (WHO, 2004). It is bland and

flavorless due a combination of very low salt content and similarly low values of calcium and bicarbonate ions. In large-scale municipal settings, desalinated water is often treated with calcium and magnesium and carbonated with carbon dioxide to reduce aggressivity and also to help with taste (Ludwig, 2004). Desalinated water may be more subject to microbial growth problems than other waters as a result of: higher initial temperature (from treatment process) and high temperature (application in hot climates) (WHO, 2004).

3.2.1 Ionogenic Composition

For practical purposes the concentrations of alkalinity and carbon dioxide in the distillate are negligible. In the table below pH is understood to be 6.0-6.3 and CO_2 is less than 1 ppm, at 28^{o} C.

Table 1: Product composition of different seawater desalination processes (seawater salinity 32 gl^{-1}) as presented in Ludwig's research (2004).

		RO		MSF
Parameter	**Unit**	**1st Stage**	**2nd Stage**	
Sodium	mg/l	72.8	1.6	7.1
Potassium	mg/l	4.8	0.2	
Calcium	mg/l	1		0.4
		Product Composition		
Magnesium	mg/l	3.8	0.1	
Chloride	mg/l	122.7	2.6	11
Sulfate	mg/l	7.4	0.1	
Nitrate	mg/l	1.1	0.1	
Alkalinity	mg/l	1.4		0.7
Silica	mg/l	0.2		
Carbon Dioxide	mg/l	20	20	0.5
TDS	mg/l	215.2	4.7	19.2

Because of the high effectiveness of these processes, they are frequently used with only a low level of residual disinfectant. However, the absence of multiple barriers like filters or ultraviolet treatment, places stress on the continuously safe operation of a stand-alone process and implies that even a short-term decrease in effectiveness may present an increased risk to human health.

3.2.2 Heavy Metal Composition

Surface water generally contains a broad range of heavy metals, however, only in trace concentrations. Thermal desalination processes have been shown to very effectively reduce common heavy metal concentrations of seawater.

Table 2: Heavy metal concentration in Arabian Gulf water and in the distillate of MSF plants at various Saudi Arabian dual-purpose installations 1992-1994 (Mayankutty et al. 1995) as seen in Ludwig's research (2004).

	Heavy Metals Concentrations (µg/l) in				
	Seawater			**Product water of MSF Plants**	
Element	**Min**	**Max**	**Mean**	**Min**	**Max**
Arsenic	ND - 1.2	5.6 - 7.2	2.6 - 3.3	ND	0.77-18
Calcium	ND - 0.3	1.3 - 1.5	0.08 - 1.0	ND	1.0 - 1.3
Chromium	ND	ND	ND	ND	ND
Mercury	ND - 0.4	0.1 - 1.8	0.04 - 0.17	ND	0.3 - 2.8
Lead	ND	ND	ND	ND	ND
Selenium	ND	0.75 - 0.96	0.20 - 0.33	ND	0.52 - 0.67

3.2.3 Organic Composition

As previously mentioned RO and MSF processes are highly effective. Organic compounds found in feedwater can be removed by more than 95 percent the distillate. However, specific organic pollutants from industrial, oil, and chemical discharge spills, comprise vapor volatile constituents. These are set free during vapor flashing and can dissolve in the condensing distillate. These compounds are mainly low boiling point aliphatic and aromatic hydrocarbons like methane, ethane, propane, and aromatic compounds like benzene, xylenes, and phonels. During disinfection higher molecular weight and less volatile substances are formed. Chlorinated and bromated hydrocarbons like chloro- and bromo- methanes, ethanes, and halogenated aromatics are of similarly volatile nature. Any of the substances, if present in the feedwater, can reach the distillate via by stripping and dissolving in the distillate (Ludwig, 2004). Fortunately, these concentrations are generally at or below drinking water standards and pose virtually no risk to users.

4. Bromine Chemistry

4.1 History

Bromine is the only liquid nonmetallic element. It is a member of the halogen group. At room temperature it is a heavy, volatile, and dangerous reddish liquid. It is naturally occurring in seawater and the Earth's crust. Bromine has a pungent odor and is irritating to the skin, eyes, and respiratory systems. Exposure to concentrated bromine vapor may be fatal.

4.2 Bromine in Solution

Bromine is an oxidizer and easily dissolved in water. When added to water, bromine forms hypobromous acid. As a weak acid, HOBr partly dissociates to form hydrogen ions and hypobromite ions. The relative quantities of each are dependent on the pH of the solution. When pH is between 6.5 and 9 both hypobromous acid and hypobromite ions are present. If water contains ammonia nitrogen, bromamines will form (NH_2Br, $NHBr_2$, and $NHBr_3$).

Knowing when hypobromous acid (HOBr) disassociates into hypobromite ion (OBr^-) is important because that is the point at which bromate (BrO_3^-) begins to form.

$$K_a = \frac{[OBr^-][H^+]}{[HOBr]} \tag{4.2.2}$$

To understand the relative amounts of $Br_{2(aq)}$, Br_3^-, HOBr, and OBr^- in a solution, it is helpful to construct a predominance diagram. Consider a predominance area diagram from aqueous bromine species at 25^0C in which the diagram axes are pH and the negative log of the bromide concentration. Lines representing equality of concentration between significant species are sought in the form of equations containing $[Br^-]$ and pH.

The overall reactions relating to the bromine species of interest are:

1. $Br_{2(aq)} + H_2O \rightleftharpoons HOBr + H^+ + Br^-; K_h = 6x10^{-9}$
2. $HOBr \rightleftharpoons OBr^- + H^+; pK_a = 8.48$
3. $Br_{2(aq)} + Br^- \rightleftharpoons Br_3^-; K = 15.9$

The predominance area diagram is shown below in Figure 1 and demonstrates that at pH greater than 8.48, the solution is dominated by OBr^-.

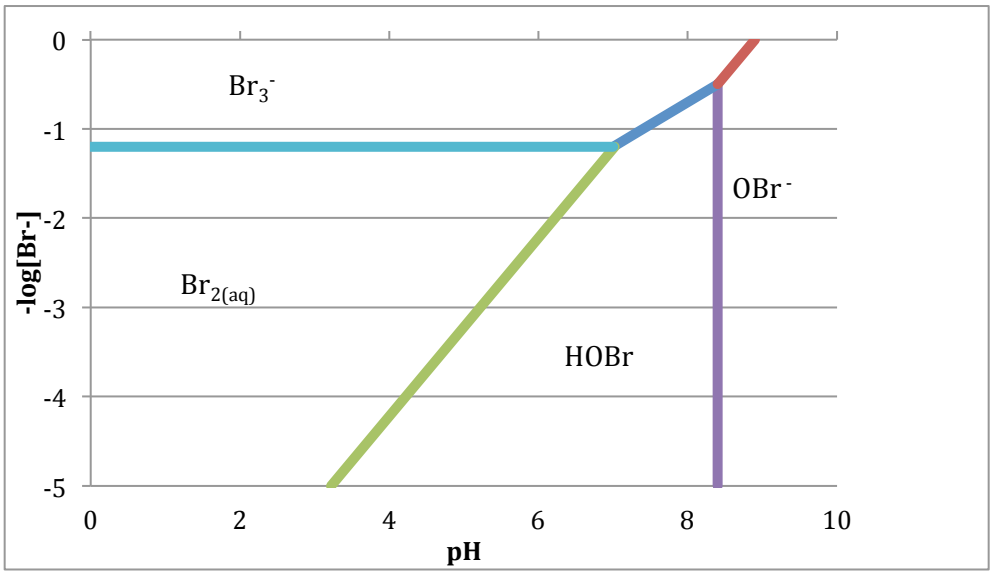

Figure 1: Predominance area diagram for aqueous bromine species at 25^0C. Adapted from Snoeyink and Jenkins, 1980.

In addition to predominance diagrams, distribution diagrams are helpful for understanding bromine species' behavior in solution. Multiplication of the analytical concentration by the appropriate ionization fraction at a particular pH value will directly produce the concentration of the species at that pH (Snoeyink, 1980). The alphas shown below in Figure 2 on bromine's distribution diagram are: $\propto_{Br_2} = \frac{[Br_2]}{C_{T,Br}}$, $\propto_{HOBr} = \frac{[HOBr]}{C_{T,Br}}$, and $\propto_{OBr^-} = \frac{[OBr^-]}{C_{T,Br}}$.

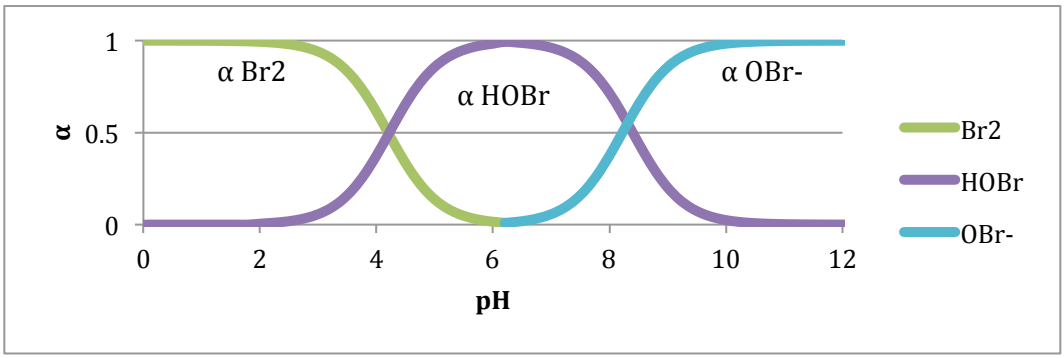

Figure 2: $[Br-] = 10^{-4}M, C_{T,Br} = [Br_2] + [HOBr] + [OBr^-]$, adapted from Snoeyink and Jenkins, 1980.

4.3 Bromate

If bromate is going to form from the oxidation of bromide, it is generally accepted that this proceeds via an intermediate reactive bromine species (White, 1986, Williams et al., 1978). These species can be dibromine, hypobromous acid, and hypobromite ion. Dibromine (Br_2), as demonstrated in Figures 3 and 4, is only significant at pH 5.5 and lower. Managing the equilibrium between $HOBr$ and OBr^- is essential to controlling bromate formation (Haag and Hoigne 1983).

Because the hypobromite ion is the main pathway by which bromate forms, $3OBr^- \leftrightharpoons 2Br^- + BrO_3^-$, pH is the obvious control method. It can be manipulated to drive bromine equilibrium towards hypobromous acid, which is unlikely to further oxidize to bromate. On a somewhat negative note hypobromous acid is much more inclined to combine with organic compounds than the hypobromite ion (Tynan, 1993). However, there is so little organic material left at the distillate end of a properly operating RO or MSF that it is not expected to be a serious trade-off.

Sayoto et al (1990) found that increasing bicarbonate concentration reduced reactive bromine formation. At pH 8, increasing alkalinity caused an increase in bromate formation, whereas at pH 7, increasing alkalinity reduced bromate formation (Krasner et al., 1993). Carbonate and bicarbonate act as scavengers of radical species (Langlais et al., 1991). Therefore, it would make sense that increasing alkalinity would decrease bromate by quenching radicals. In this case, the effects of alkalinity on bromate are not completely understood.

Haag and Hoigne (1983) found that ammonia would react with reactive bromine to form monobromamine, which would then slowly react to form nitrate

and bromide. Ammonia, at a concentration of 50 µg/l caused a lag in bromate formation in a computer simulation (von Gunten and Hoigne, 1992). Only after most of the ammonia was depleted did bromate form. The reaction with ammonia was the dominant sink for reactive bromine in the system. Yet, Krasner et al. 1991, found that ammonia was ineffective at reducing bromate formation at pH<8.0.

4.3.1 Use of bromate on ships

In the 1990's, the Navy hired a research company--Novatek--to evaluate whether or not bromate was forming in shipboard drinking water. Assuming that the average pH of desalinated water was between 5.0 and 6.0, Novatek tested for bromate in water ranging up to 7.5 pH. No bromate was observed during the course of their study. This is as predicted given bromine's chemistry and reactions in solution (Figure 1 and Figure 2). Table 3 gives a breakdown of expected dis~~as~~sociation percentages for varying pH's.

Based on data collected from Coast Guard Cutters' patrols spanning 2008-2012, rarely is a ship's water at a pH between 5.0-6.0. The average is closer to 7.0, with several ships seeing sporadic pH's higher than 8.0. It is reasonable to assume that when a ships' water supply pH exceeds 8.0 bromate is present.

Table 3: Distribution of of bromine as hypobromous acid and hypobromite ion, using pKa = 8.48

% of bromine as HOBr	pH	% bromine as Obr-
99.7	6.0	0.3
99.0	6.5	1.0
96.7	7.0	3.3
89.6	7.5	10.4
67.0	8.0	33.0
0.3	8.5	99.7

4.3.2 Theoretical bromate concentration estimates

The potential concentration of bromate in solution as a function of pH can be calculated using the following method.

$$\Delta G_{BrO_3^-} = 1.67\ \frac{kJ}{mol} \tag{4.3.1}$$

Equilibrium calculations for adding Br_2 to water assuming the following reaction:

$$3Br_{2(aq)} + 3H_2O \rightarrow BrO_3^- + 5Br^- + 6H^+ \tag{4.3.2}$$

$$\mathrm{K} = \frac{[BrO_3^-][Br^-]^5[H^+]^6}{[Br_2]^3} \tag{4.3.3}$$

Using, $\Delta G^0 = -RTlnK$ and the following to determine K:

$$\Delta BrO_{3-} = 1.67\ \frac{kJ}{mol}, \Delta G_{Br^-} = -104\frac{kJ}{mol}, \Delta Br_{Br_{2(aq)}} = 18.98\frac{kJ}{mol},$$

$$\Delta G_{H^+} = 0\frac{kJ}{mol}, \Delta G_{H_2O} = -237.18\frac{kJ}{mol}, \tag{4.3.4}$$

Then, $\Delta G =$

$$(1\ mol)\left(1.67\frac{kJ}{mol}\right) + (5\ mol)\left(-104\frac{kJ}{mol}\right) - (3\ mol)\left(18.98\frac{kJ}{mol}\right) -$$

$$(3\ mol)\left(-237.18\frac{kJ}{mol}\right) = 136\ kJ \tag{4.3.5}$$

When $R = 8.314\frac{J}{molK}$ and $T = 298\ K$,

$$lnK = -\frac{\Delta G^0}{RT} = \frac{-136.27x10^3\frac{J}{mol}}{8.314\frac{J}{molK}\,x\ 298\ K} = -0.056,\ K = e^{-55} \tag{4.3.6}$$

$$K = \frac{[BrO_3^-][Br^-]^5[H^+]^6}{[Br_2]^3} = e^{-0.55} \tag{4.3.7}$$

For the solution pH =6, 7 and 8 the following equilibrium exist. This indicates that the concentration of bromate and bromide increase significantly as the pH increases.

$$K = \frac{[BrO_3^-][Br^-]^5}{[Br_2]^3} = \frac{e^{-55}}{[H^+]^6} = \frac{e^{-55}}{[10^{-6}]^6} = 1.3x10^{12} \quad (4.3.8)$$

$$K = \frac{[BrO_3^-][Br^-]^5}{[Br_2]^3} = \frac{e^{-55}}{[H^+]^6} = \frac{e^{-55}}{[10^{-7}]^6} = 1.3x10^{18} \quad (4.3.9)$$

$$K = \frac{[BrO_3^-][Br^-]^5}{[Br_2]^3} = \frac{e^{-55}}{[10^{-8}]^6} = \frac{e^{-55}}{[10^{-8}]^6} = 1.3x10^{24} \quad (4.3.10)$$

Fix the bromine concentration at 0.1 mg/L

Br_2 MW = 160 gm. 0.1 mg/L gives a molarity of (0.1 mg/L)/ 160 gm/mol = 6.25 x 10^{-6} mols/L

$$K = \frac{[BrO_3^-][Br^-]^5}{[Br_2]^3} = \frac{e^{-55}}{[H^+]^6} \quad (4.3.11)$$

For the reaction: $3Br_{2(aq)} + 3H_2O \rightarrow BrO_3^- + 5Br^- + 6H^+$,

If $X = \left[BrO_3^-\right]$ then $\left[Br^-\right] = 5X$

$$\frac{[X][5X]^5}{[6.25x10^{-6}\frac{mol}{L}]} = \frac{e^{-55}}{[H^+]^6} \quad (4.3.12)$$

$$X = \left(\frac{\left(e^{-55}x\left(6.25x10^{-6}\right)^3\right)}{[H^+]^6x5^5}\right)^{\frac{1}{6}} \quad (4.3.13)$$

For pH = 6 X = 0.0683 $\frac{mol}{L}$

For pH = 7 X = 0.683 $\frac{mol}{L}$

For pH = 8 X = 6.83 $\frac{mol}{L}$

These calculations do not take into account the conversion of $Br_{2(aq)}$ to HOBr and Br^-:

$$Br_{2(aq)} + H_2O = HOBr + H^+ + Br^- \qquad (4.3.14)$$

In addition reaction kinetics are not considered in the calculations.

However, the trend that indicates more BrO^-_3 as pH rises is shown clearly. The reported Gibbs Free Energy values reported in the literature for some of the Br compounds are variable but the pH trends shown here are consistent. In addition the free energy value for $Br_{2(l)}$ was used as the input form of Br. However, the Br is typically added from an ion exchange reaction for which Br free energy is not available.

. Novatek's study (Gilbert, 1996) indicated that there was no bromate presence in solutions with pH up to 7.5. Reaction kinetics were not considered in this study. A similar study should be conducted at pH 8.0-9.0 to learn the expected concentration of bromate, because theoretical calculations indicate that somewhere between pH 7.0 and 8.0 Bromate concentration spikes well above drinking water standard levels.

4.3.3 Health Risks

The EPA's MCL for bromate is 10 µg/L or 0.01 ppm. Bromate has been listed a probable human carcinogen and causes cancer in rats. Three key studies (Kurokawa et al., 1986a, 1986b; DeAngelo et al., 1998) establish the carcinogenicity of bromate in rats. Tumors were observed at multiple sites in male rats, including: kidneys, thyroid, and sexual organs. In female rats, tumors were only observed in the kidneys. There was a clear dose response between tumor incidence and

progression of the tumors. The EPA estimates the lifetime probability of dying with a tumor induced by an average daily dose of bromate using a multistage model. Estimates of the cancer slope factor (q_{human}) derived from the frequency of tumors at a particular site are reported below in Table 3. The median and upper 95th percentile cancer slope factor estimates are provided for each tumor site and the combined sites. The corresponding LED_{10} values are provided. The LED_{10} is the lower-bound estimate of the average lifetime dose associated with a ten percent cancer risk and was calculated using:

$$LED_{10} = \frac{-\ln(0.9)}{q_{human}} \qquad 4.3.1$$

where q_{human} represents the upper 95 percent confidence bound on the q_i after correcting for difference in size between test animals and humans.

Table 4: Human cancer potency and LED_{10} values for bromate as reported by the U.S. EPA (2001)

	q_{human} (mg/kg-day)$^{-1}$		LED_{10} (mg/kg-day)$^{-1}$
Tumor Type	**Median**	**95th Percentile**	**Lower 95th Percentile**
Mesothelioma	0.27	0.54	0.2
Kidney adenoma or carcinoma	0.08	0.18	0.59
Thyroid adenoma or carcinoma	0.05	0.1	1.1
Multi-site	0.41	0.7	0.15

5. CONCLUSIONS

It is clear that the drinking water guidelines -- NSTM, Coast Guard Potable Water Manual, Manual of Naval Preventive Medicine -- need to be updated to reflect the risk that bromate presents in environments where the pH is greater than 8.0. There is no question that as pH rises so does the bromate concentration. Clear guidance should be established for handling high pH situations. While bromate is not officially listed as a human carcinogen, it is probable that it will make the list at some point in the near future. Changes also need to be made to the manuals to prevent people from drinking water brominated to greater 1.0 ppm TBR and chlorinated to 4.0 ppm FAC. Chlorine and bromine have two different sets of EPA standards. Future research should examine whether brominating or chlorinating to between 2.0 ppm and 5.0 ppm is necessary for high-risk water scenarios. Additional research might be done on the epidemiology of cancer in Coast Guard members who have served underway on ships with making capabilities.

REFERENCES

Amy, G. and Siddiqui, M.S., 1998, Strategies to control bromate and bromide.

COMDINST M6240.5, 1999, Water Supply and Wastewater Disposal Manual.

DeAngelo, A. B., George, M. H., Kilburn, S. R., Moore, T. M., Wolf, D. C., 1998, Carcinogenicity of potassium bromate administered in the drinking water to male B6C3F1 mice and F344/N rats. Toxicol Pathol 26(5), 587-94.

EPA-HQ-OPP-2009-0167, 2009, Bromine Summary Document: Registration Review Prelminary Work Plan.

GE Power & Water, Water Purification Handbook, Ch 27.

Gilbert, G., Bubnis, B., and Yeoman, A., 1996, A comparison of chlorine and bromine for oxidation/disinfection, chemical oxidation: Proceedings of the international symposium chemical oxidation, technology for the nineties, Vol 6.

Greenlee, L. F., Lawler, D. F., Freeman, B. D., Marrot, B., and Moulin, P., 2009, Reverse Osmosis Desalination: Water Sources, Technology, and Today's Challenges, Water Research, Vol 43, issue 9.

von Gunten, U. and Hoigne, J., 1992, Factors controlling the formation of bromate during ozonation of bromide containing waters. Aqua, 49, 299-304.

Haag, W.R. and Hoigne, J., 1983, Ozonation of bromide-containing waters: Kinetics of formation of hypobromous acid and bromate. Environmental Science and Technology, 17, 261-267

Health Protection Agency, 2009, Bromine Toxicological Overview.

Krasner, S. W., Gramith, J. T., Means, E. G., Patania, N. L., Najm, I. N., and Aieta, E. M., 1991, Formation and control of brominated ozone by-products. Proceedings of American Water Works Association Annual Conference 1991, Philadelphia, 934-971.

Krasner, S. W., Glaze, W. H., Weinberg, H. S., Daniel, P. a., and Najim, I. N., 1993, Formation and control of bromate during ozonation of waters containing bromide, Journal of the American Water Works Association, 85, 73-81.

Kurokawa, Y., Aoki, S., Matsushima, Y., Takamura, N. and Hayashi, Y. 1986a, Dose-response studies on the carcinogencitiy of potassium bromate in F-344 rats after long-term oral administration. Journal of the National Cancer Institute, 77, 977-982.

Kurokawa, Y., Takayama, S., Konishi, Y., Hiasa, Y., Asahina, S., Takahashi, M., and Hayashi, Y., 1986b, Dose-response studies on the carcinogenicity of potassium bromate in F-344 rats after long-term oral administration, Journal National Cancer Institute, 77(4), 977-982.

Kurokawa, y., Matsushami, Y., Takamura, M., Imazawa, T., and Hayashi, Y., 1987, Relationship between the duration of treatment and the incidence of renal cell tumors in F-344 rats administered potassium bromate. Japanese Journal of Cancer Research (Gann), 78, 358-364.

Langlais, B., Reckhow, D. A., and Brink, D., R., 1991, Ozone in water treatment: Applications in engineering. American Water Works Association.

Lewis, G., and Randall, M. 1916, The free energy of bromine compounds. Journal of the American Chemical Society, 38 (11), 2348-2356.

Ludwig, H., 2004, Composition of desalinated water, Common fundamentals and unit operations in thermal desalination systems, Vol II, Enclyopedia of desalination and water resources.

NAVMED P-5010-6, 2005, Manual of Naval Preventive Medicine, Ch 6 Water Supply Afloat.

NSTM CH 533, 1995, Naval Ship's Technical Manual Chapter 533.

Sayato, Y., Nakamuro, K., Hayashi, M. and Sano, H., 1990, Formation of active bromine from bromide ion by aqueous ozonation. Chemosphere, 20, 309-315.

Snoeyink, V. L. and Jenkins, D. 1980, Water Chemistry.

Tarr, M. A. , 2003, Chemical Degradation Methods for Wastes and Pollutants: Environmentl and Industrial Applications.

Tynan, P. J., Lunt, D. O., and Hutchinson, J, 1993, Formation of Bromate During Drinking Water Disinfection, Department of Energy.

U. S. EPA RED Facts, 1993, Bromine. Washington, DC, US Environmental Protection Agency

U.S. EPA 2001, Stage 2 occurrence and exposure assessment for disinfectants and disinfection by products (D/DBPs). Washington, DC, US Environmental Protection Agency.

Water Wastes Digest, 2003, Brominated Resins, http://www.wwdmag.com.

White, G.C., 1986, Chlorine dioxide handbook of chlorination, 2nd ed, 833-892.

Wiley, J. & Sons, 2005, Analytical Methods for Drinking Water: Advances in Sampling and Analysis.

Williams, P.M., Baldwin, R. J. and Robertson, J., 1978, Chlorination of sea-water: Preliminary observations on the oxidation of bromide, chloride, and organic carbon. Water Research, 12, 385-388.

World Health Organization, 2004, Guidelines for Drinking Water Quality: Recommendations, Vol 1.